THE OXIDE ELECTRODE, AN INDICATOR FOR EDTA IN THE AMPEROMETICAL TITRATION OF METAL IONS

The Thallium(III)-oxide-Electrode, the Nickel-(III)-oxide-Electrode and the Cobalt(III)-oxide-Electrode

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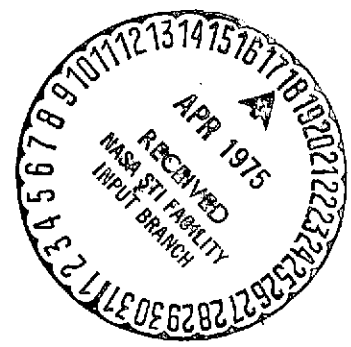

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16. Abstract

The equivalence point in chelatometric titrations can be indicated amperometrically if a pin of platinum coated with an oxide is used as anode and bright platinum as the cathode. A voltage of 0.8 to 1.0 volts is applied to the electrodes. The current flowing between the electrodes increases very much if there is excess EDTA in the solution. The following oxides are suitable for coating the anode: thallium(III) oxide, nickel(III) oxide and cobalt(III) oxide. The titration curve is either V-shaped or angular, according to the cation.

The behavior of these oxide electrodes was investigated. The indication depends on the acidity of the solution. The highest indication is found at pH 3.5 to 5, and also at pH 10. The method presented is applicable for determining various metal ions.

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THE OXIDE ELECTRODE, AN INDICATOR FOR EDTA IN THE AMPEROMETICAL TITRATION OF METAL IONS

The Thallium(III) Oxide Electrode, the Nickel(III) Oxide Electrode and the Cobalt(III) Oxide Electrode

Gerald Kainz, Gerhard Sontag and Hermann A. Müller

We recently found [1] that certain metal chelates, / 127* added to the titration solution in a small amount, make possible the amperometric indication of excess EDTA (after the equivalence point). We established the cause of this to be the fact that an extremely thin oxide film forms on the platinum anode under the effect of the applied polarization voltage. This oxide reacts with EDTA, so that the current flowing between the electrodes rises steeply.

It must be emphasized that a very minute amount of oxide, some $1 \cdot 10^{-6}$ g, is sufficient for the current-generating process at the anode. The following metal chelates were active in this sense: lead(II)-EDTA, manganese(II)-EDTA and thallium(I)-EDTA. The metal chelates listed were added to the sample solution in quantities of $5 \cdot 10^{-7}$ mole. The oxide layer formed during the titration.

It appeared desirable to avoid these active additives and to prepare an electrode covered with an oxide layer from the beginning. This oxide electrode would then be used as the anode

* Numbers in the margin indicate pagination in the original foreign text.

with respect to a plain platinum cathode in the amperometric titration of metal ions with EDTA.

In this work, we have coated electrodes with layers of thallium(III) oxide, nickel(III) oxide, and cobalt(III) oxide, respectively. The properties of these oxide electrodes for indication of excess EDTA were studied. It appeared that such electrodes make a quite outstanding indication of EDTA possible.

I. The Thallium(III) Oxide Electrode

Preparation. Two platinum electrodes were immersed in a 0.001 M thallium(I) nitrate solution and electrolyzed for 10 minutes at pH 10 with a current of 5 μA. A few micrograms of yellow-brown Tl_2O_3 deposited.

The Tl_2O_3 electrode was connected with a plain platinum electrode in the solution of the metal ion to be determined, and a polarization voltage of 1.1 V was applied. The current between the electrodes was constant after 5 minutes.

We observed two types of titration curves in the titrations with EDTA: a) if the metal ion to be determined was reduced at the platinum cathode we obtained a V-shaped titration curve (example: Cu^{2+}, pH 10). The decreasing branch was due to the decrease in the metal ion concentration (due to complexing with EDTA). The rising branch (after the equivalence point) was caused by excess EDTA. b) if the metal ion to be determined was not reduced at the platinum cathode, we obtained an angular curve. The current remained approximately constant up to the equivalence point. After the equivalence point, free EDTA was indicated (example: Ca^{2+} at pH 10). / 128

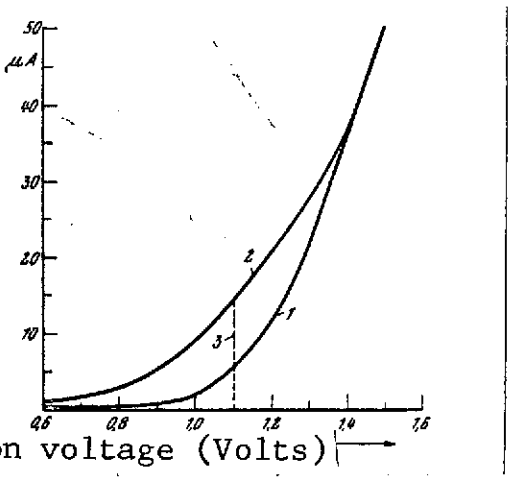

Figure 1. Determination of the optimum polarization voltage. Electrodes: Pt/Pt-Tl_2O_3; pH 10.

1: current-voltage curve for the buffer
2. current-voltage curve for the buffer with 0.20 ml EDTA (0.01 M)
3. optimal polarization voltage.

Thus, the Pt(cathode)-Pt-Tl_2O_3(anode) indication system makes possible the direct indication of EDTA, independent of whether or not the metal ion to be determined is indicated at the platinum cathode. Now it was of interest to investigate the conditions of use for the Tl_2O_3 electrode in more detail.

a) Effect of the applied polarization voltage

We desired to determine the polarization voltage which must be applied at the electrodes to obtain a maximal signal for EDTA. For this, we immersed the electrode pair described in a buffer solution (pH 10), and applied a constant voltage, beginning with 0.6 V. The current flowing through the buffer solution was measured. Then 0.20 ml 0.01 M EDTA was added and the increase in current determined. Figure 1 shows that the

optimal signal for EDTA is obtained between 1.0 and 1.1 V. When the polarization voltage is increased, the EDTA signal becomes smaller, and is practically zero at 1.4 V.

b) Effect of the solution pH /129

We found that the current increase due to EDTA depends very strongly on the solution pH (Figure 2). The indication begins at pH 2.5 and ends at pH 11. In between there are two maxima (at pH 5 and 10) as well as a minimum (at pH 8).

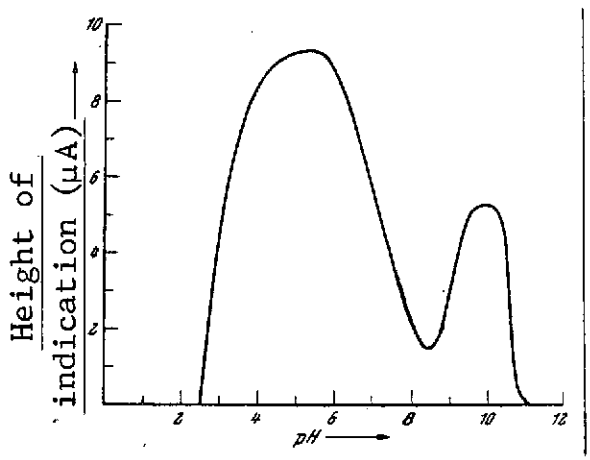

Figure 2. Dependence of the magnitude of the indication on the solution pH. Tl_2O_3 electrode. Indication magnitude for 0.20 ml 0.01 M EDTA.

In particular, we must mention that the Tl_2O_3 electrode was slowly dissolved by the buffer solution (acetic acid - sodium acetate) between pH 2.5 and pH 6, so that it is usable for only one or two titrations and then must be reformed. This was unfortunate, because the indications in the acid region are almost twice as great as in the alkaline range. Later we found that the acetic acid used is responsible for the dissolution of the electrode. As is well known, acetic acid forms relatively stable, soluble acetate complexes with certain trivalent ions.

When we used another buffer (e. g., potassium hydrogen phthalate with HCl or NaOH) the oxide layer was maintained.

II. The Nickel(III) Oxide Electrode

Preparation. Two platinum electrodes were immersed in a 0.001 M nickel nitrate solution containing some sodium acetate. The anode was coated with a nickel(III) oxide layer at a current of 10 μA (duration: 10 minutes). 5 μg of black Ni_2O_3 deposited.

Ammonia-ammonium chloride was not suitable as a buffer for the forming; no oxide formation occurred. Ammonia forms a relatively stable tetrammine complex with Ni^{2+}.

a) Optimal polarization voltage / 130

This is 0.95 V (Figure 3). If a higher polarization voltage, such as 1.2 V, is applied, no indication of EDTA occurs (determined with 0.20 ml of a 0.01 M solution).

b) Dependence on the solution pH

A signal for EDTA is obtained between pH 2.5 and pH 11.5 (Figure 4). Maxima appear at pH 3.5 and 10. The minimum for the indication is at pH 8, as it is for the Tl_2O_3 electrode.

In particular, it should be noted that the electrode is sensitive to acetic acid between pH 2.5 and 5. It is rapidly dissolved by an acetate buffer, and then does not indicate EDTA below pH 5. The cause of this is the formation of a soluble acetate complex of Ni^{3+}. In the experiments of Figure 4, therefore, we used potassium hydrogen phthalate (with HCl or NaOH) as the buffer.

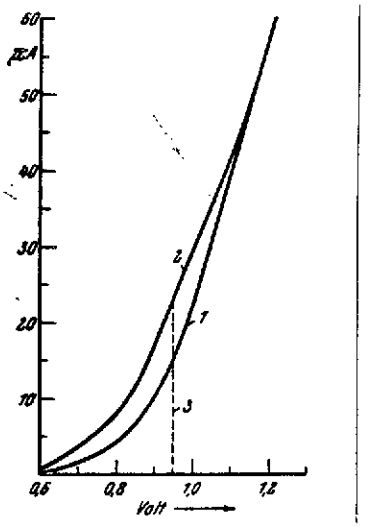

Figure 3. Determination of the optimal polarization voltage. Electrodes: Pt/Pt-Ni_2O_3; pH 10.

1. current-voltage curve for the buffer
2. current-voltage curve for the buffer with 0.20 ml of 0.01 M EDTA.
3. optimal polarization voltage.

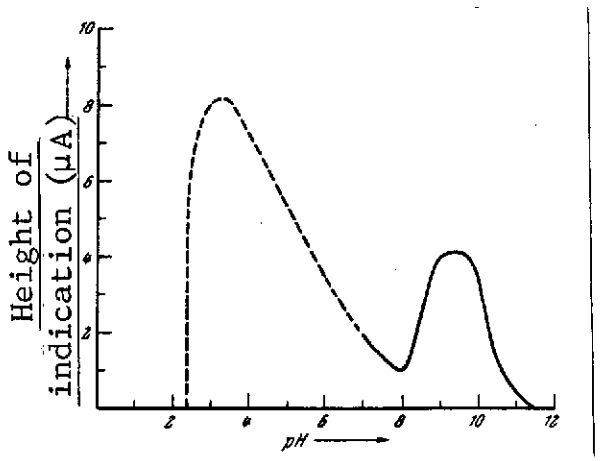

Figure 4. Dependence of the magnitude of indication on the solution pH. Ni_2O_3 electrode. Indication magnitude for 0.20 ml of 0.01 M EDTA.

The electrode is also sensitive to excess EDTA between pH 2.5 and pH 6: Ni_2O_3 slowly dissolves. A single indication of EDTA is possible, however; then the electrode must be reformed. The Ni_2O_3 electrode is stable at about pH 10, though, and can be used for many titrations. The range for single application was dashed in Figure 4, while the stable range was shown by a solid line.

We also studied the behavior of the Ni_2O_3 electrode at pH 8 in more detail. The minimum indication occurs there. We found a hint when we determined the signal height as a function of the amount of EDTA added (at various pH values). /131

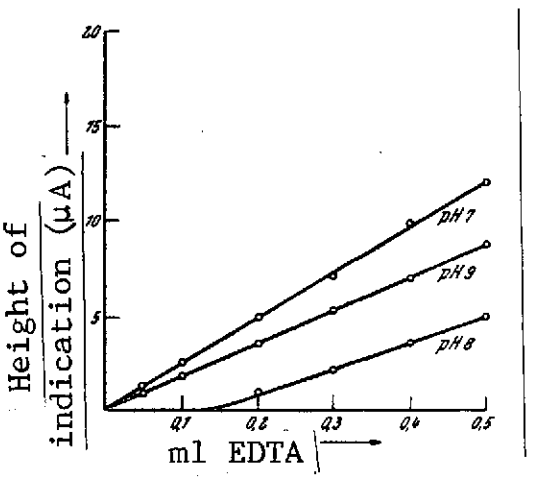

Figure 5. Dependence of the height of the indication on the amount of EDTA (0.01 M) added at different pH values. Ni_2O_3 electrode at 0.9 V.

The first series of experiments was carried out at a polarization voltage of 0.9 V (Figure 5). It can be seen that a certain amount of EDTA (0.13 ml) must be added at pH 8 before a rise in current (= indication) occurs. At the other pH values, by contrast, the electrode responds immediately to the EDTA.

We also performed the same series of experiments at a polarization voltage of 1.2 V (Figure 6). A slight no-response consumption is already present at pH 7. The no-response consumption is greatest at pH 8 (0.20 to 0.25 ml 0.01 M solution) and then decreases again. It is about 0.12 ml at pH 9.

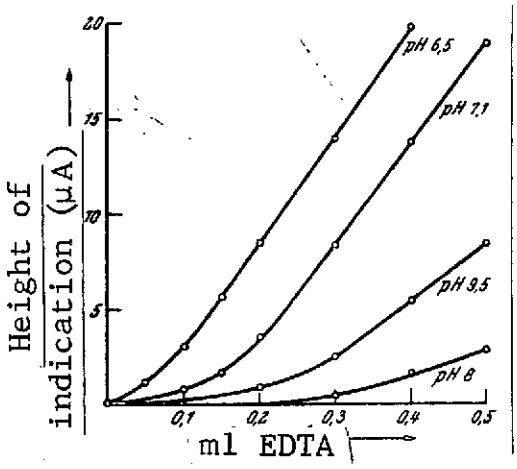

Figure 6. Dependence of the height of the indication on the amount of EDTA at different pH values. Ni_2O_3 electrode. Polarization voltage: 1.2 V.

We can say, therefore: no-response consumption of EDTA occurs: a) if the polarization voltage is too high (e. g., 1.2 V); b) at pH 8 we cannot avoid no-response consumption of EDTA even at a polarization voltage of 0.9 V. Therefore, the analytical application of the Ni_2O_3 electrode can be recommended only for pH 10 (at a polarization voltage of 0.9 V).

III. Cobalt(III) Oxide Electrode

Preparation. 0.001 M cobalt(II) nitrate solution was buffered at pH 7 with ammonium acetate. Two platinum electrodes were immersed, and a constant current of 5 μA was applied for 5 minutes. 1.4 μg of Co_2O_3 deposited on the anode. The

suitability of the electrode pair, Pt(cathode) - Pt-Co_2O_3 (anode), for the indication of EDTA was investigated.

a) Dependence on the polarization voltage

The curve obtained is similar to that for Ni_2O_3 (see Figure 3). The optimum polarization voltage is somewhat lower though (0.75 to 0.8 V). This voltage is also recommended for analytical application.

In comparison, 1.2 V is already too high. At pH 10, for instance, 0.20 ml 0.01 M EDTA is no longer indicated. A signal appears only with large additions of EDTA. Thus, Co_2O_3 behaves like Ni_2O_3. / 133

b) Signal height and solution pH

EDTA is indicated by Co_2O_3 between pH 2.5 and 11 (polarization voltage: 0.8 V). The maxima for the indication are at pH 3.5 and 10. A minimum appears at pH 8.

Like the Tl_2O_3 and Ni_2O_3 electrodes, the Co_2O_3 electrode is sensitive to acetic acid between pH 2.5 and pH 6. This slowly dissolves the oxide layer. But the Co_2O_3 electrode differs from the Ni_2O_3 electrode in being stable toward EDTA over the entire range, and can, therefore, be used for many titrations.

Now it was necessary to test whether no-response consumption of EDTA occurs under certain conditions (pH, polarization voltage). It does in fact exist:

a) at 0.8 V polarization voltage; the no-response consumption reaches a maximum at pH 8 (see Figure 7).

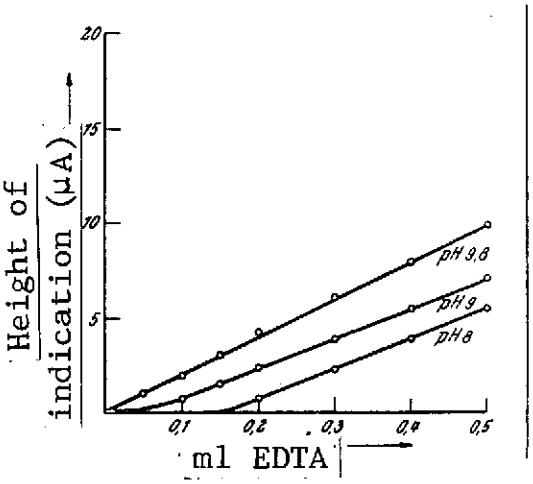

Figure 7. Dependence of the height of indication on the amount of EDTA added at different pH values. Co_2O_3 electrode. Polarization voltage: 0.8 V.

b) at 1.2 V polarization voltage: the no-response consumption is significantly higher than that under a) and extends over a greater pH range (from about pH 6 to 12).

c) Analytical application / 134

If a polarization voltage of 0.8 V is maintained, one can work with a Co_2O_3 electrode in the range of pH 2.5 to 6.5 and pH 9 to 11. The region of the minimum should be avoided in any case, as should a polarization voltage higher than 0.8 V. Acetate buffer should also be avoided, because it causes slow dissolution of the oxide layer (below pH 6), so that the electrode must be reformed after a few determinations.

IV. Explanation of the Course of the Reaction

The preceding study raised some questions which had to be considered. These were:

1. Cause of the indication

A redox reaction occurs between EDTA and the oxide. First, EDTA reduces part of the oxide. The reduced sites on the oxide film are continuously oxidized anodically. The electrons liberated in this reaction are indicated by the measuring instrument and are an extremely sensitive indicator for free EDTA.

The amount of substance reacting at the electrode is extremely minute. The total amount of oxide at the anode is only about $5 \cdot 10^{-6}$ g. No visual change or dissolution of the oxide can be observed during the reaction.

2. Cause of the maxima and the minimum in the height of indication

On this we must say: The oxides are resistant between pH 2.5 and pH 11, and do not change chemically. The differing extent of the reaction must, then, be due to the EDTA. Depending on the pH, the EDTA occurs in different dissociation stages. Three reactions come into question:

a) pH 9 to 11: The conversion, and with it, the signal height, rises from pH 8 to 10. There is a maximum at pH 10. The concentration of Y^{4-} also increases in the same manner (Table 1). Now it is known that amines are relatively easily oxidized to the corresponding amine oxides. Amine salts, in contrast, are oxidizable only with difficulty.

b) pH range about 8: A minimum in the indication, as well as no-response consumption of EDTA, occurs here. At pH 8, HY^{3-} is almost exclusively present. It appears, first, that this dissociation form is bound at the Ni^{3+} or Co^{3+} surface in much smaller amount, and that the further access of EDTA is sterically hindered. The increase in the no-response consumption also suggests this, if one increases the polarization voltage / 135 (increased accumulation of HY^{3-} about the anode).

Table 1.

Dissociation Form	pH 2	3	4	5	6	7	8	9	10	11	12
Y^{4-}	-	-	-	-	-	-	1	6	37	84	98
HY^{3-}	-	-	-	7	43	87	98	94	63	16	2
H_2Y^{2-}	7	67	95	93	57	13	1	-	-	-	-
H_3Y^{-}	46	30	5	-	-	-	-	-	-	-	-
H_4Y	47	43	-	-	-	-	-	-	-	-	-

c) Ph between 2.5 and 7: In this range, EDTA occurs as the amine salt, with the dissociation form H_2Y^{2-} predominating. The EDTA carboxyl groups may be attacked in the reaction with the oxide. From Figures 2 and 4 we see that the signal, and, with it, the conversion, is higher, the more acidic the solution is. This also agrees with the fact that the redox potential of oxides increases with increasing hydronium ion activity. The dissolution of the oxide limits the rise in the acid range.

V. Analytical Application of the Oxide Electrodes

All three oxide electrodes are outstanding indicator electrodes in amperometric titration of metal ions with EDTA. Tl_2O_3 is recommended for the pH range of 2.5 to 11, with the

range of about 4.5 to 10 being preferred. The same is true for Co_2O_3. On the other hand, Ni_2O_3 is usable only about pH 10.

These electrodes are not suitable for pH 1 to 2, where the trivalent and tetravalent metal ions are usually titrated. At present, we are working on development of oxide electrodes for this range.

Experimental

Reagents: Forming solutions: 0.001 M thallium(I) nitrate, 0.001 M nickel(II) nitrate, 0.001 M cobalt(II) nitrate.

Apparatus: Metrohm E 261 polarograph for generating the polarization voltage and for measurement of the diffusion current; Metrohm E 456 polarizer for forming the electrodes; Metrohm EA 210 double platinum electrode.

Preparation of the oxide electrodes: The double platinum electrode is immersed in one of the solutions specified above. After adjustment of the pH (see above), the corresponding oxide is deposited on the platinum anode. The constant current (5 or 10 μA) is taken from the polarizer for 5 to 10 minutes. / 136
The electrodes can be used for many titrations.

Titration: The electrode pair, Pt(cathode)-Pt-oxide(anode) is immersed in the sample solution. Buffer is added and the optimal polarization voltage is applied. Then one waits for five minutes until the base current is constant. The sensitivity of the polarograph is set according to the magnitude of the base current: 1 to 5 · 10^{-8} A/mm for a base current of 5 μA, 1 · 10^{-7} A/mm and 1 · 10^{-6} A/mm for a base current of 20 to 30 μA. Then one titrates with 0.01 M EDTA solution reading the currents. The titration curve can also be plotted with the Polarecord.